

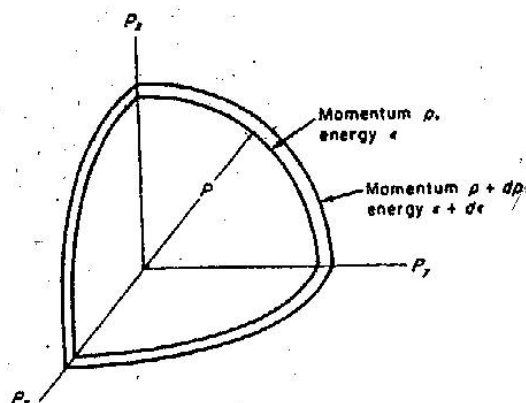
However, from (5.2-18)

$$p \, dp = m \, d\varepsilon, \quad (5.2-20)$$

whereby

$$dV_p = 4\pi p \cdot m \, d\varepsilon = 4\pi m \sqrt{2m\varepsilon} \, d\varepsilon. \quad (5.2-21)$$

FIGURE 5.1. Spherical surfaces corresponding to constant energies ε and $\varepsilon + d\varepsilon$ plotted in the momentum space (p_x, p_y, p_z) of a particle.



The number of quantum states to be found in this volume of momentum space is determined simply by dividing this result by the volume of momentum space associated with a single quantum state as given by (5.2-17). The result,

$$g(\varepsilon) \, d\varepsilon = \frac{8\sqrt{2\pi}V}{h^3} m^{3/2} \sqrt{\varepsilon} \, d\varepsilon, \quad (5.2-22)$$

is by definition the density of states factor referred to in (5.2-1). This result, of course, refers only to free particles subject to instantaneous collision interactions only. For other systems, particularly where long range mutual interactions between particles are involved, the density of states factor would be much more complex. Also, the result (5.2-22) pertains, strictly speaking, only to a container in the shape of a rectangular solid. However, since only the volume of the container appears in the final result, it is intuitively clear that the same density of states would be obtained for a container of like volume independent of its shape. This can indeed be shown to be true.

5.3 THE MAXWELL-BOLTZMANN DISTRIBUTION

If there are no restrictions on the amount of energy or momentum a particle of the system may possess, then the probability associated with all quantum states is the same, and the average number of particles per quantum state will be independent of energy. This means that the distribution function $f(\varepsilon)$ will be constant. This rather simple situation is not very important physically, since a system which is thermally

isolated from its surroundings must obey the restriction that the sum of the energies of all the particles of the system be constant, and it is systems of this type with which we shall have to deal. In this more realistic case the proportion of particles occupying states of extremely high energy is reduced and the distribution function is no longer constant with respect to energy.

To find out just what the distribution function is under these conditions, we shall proceed initially along classical lines, imagining the particles of the system to be identifiable objects such as numbered billiard balls. We shall retain the framework of quantum states and energy levels, although, ignoring the Pauli exclusion principle, we shall permit any number of particles to occupy a given quantum state of the system. We shall suppose that we are dealing with an isolated system of N distinguishable particles, with constant total energy U , which may be distributed among n energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots, \varepsilon_n$. Statistically, the ensemble will have that energy distribution which corresponds to some chance distribution of particles among levels, the number in each level being given by $N_1, N_2, N_3, \dots, N_n$. Of all the chance distributions of N particles among n energy levels, some will occur with relatively high probability on a purely statistical basis, and others will be quite unlikely. This situation is analogous to the simultaneous tossing of two coins, in which the distribution (1 head, 1 tail) is more probable than the distribution (2 heads, 0 tails) or the distribution (0 heads, 2 tails). The distribution which has the maximum probability of occurrence is that distribution of particles among levels which can be realized in a maximum number of statistically independent ways. The equilibrium state of the system will then be assumed to correspond closely to this statistical distribution of particles among levels which is of maximum probability under the conditions of the problem.

The calculation of the number of ways in which identifiable particles can be distributed among energy levels of a system is equivalent to the calculation of the number of ways in which numbered objects can be distributed among a set of numbered containers. We must thus consider the problem of determining the number of ways of distributing N identifiable objects among n containers such that there are N_1 in the first, N_2 in the second, \dots , N_i in the i th, etc. This number will be proportional to the probability with which a distribution where N_1, N_2, \dots, N_n objects are in containers 1, 2, 3, \dots , n , will occur.

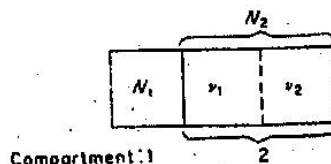
To begin, let us assume that we have only two containers in which the objects may be placed, as shown in Figure 5.2. In general there will be N_1 objects in container 1 and N_2 in container 2, with

$$N_1 + N_2 = N = \text{const.} \quad (5.3-1)$$

Let us denote by $Q(N_1, N_2)$ the number of statistically independent ways of arriving at the distribution (N_1, N_2) objects in containers (1, 2). Now $Q(0, N_2)$ is certainly equal to one, because the only way of achieving this distribution is to put all N objects into the second box, as shown in the figure. Likewise, $Q(1, N_2) = N$, because to realize this distribution, we may put object 1 in the first container and the rest in the second, object 2 in the first container, and the rest in the second, and so on through the N objects. There are N ways of choosing the object to be put in the first container and thus N ways of arriving at the distribution in question. If there are two objects in the first box, then $Q(2, N_2) = N(N-1)/2!$. This result follows because there are N ways of choosing the first object which goes into the first container, but only $N-1$ ways of choosing the second from the remaining objects; also, the two distributions

But now we may, if we wish, regard the system as having *three* distinct containers, and the total number of ways of arranging the objects so that there are N_1 in the first container, v_1 in the second and v_2 in the third [which we shall call $Q(N_1, v_1, v_2)$] will be just the product of $Q(N_1, N_2)$ and $Q(v_1, v_2)$, since for *each* arrangement (N_1, N_2)

FIGURE 5.3. The subdivision of the second container into two subcompartments, leading to a system which can be thought of as actually having been divided into *three* distinct containers.



there will be $Q(v_1, v_2)$ ways of arranging particles among the subcompartments, and there are $Q(N_1, N_2)$ basic ways of arriving at a distribution (N_1, N_2) for the two original containers. We shall find thus, that

$$Q(N_1, v_1, v_2) = Q(N_1, N_2)Q(v_1, v_2) = \frac{N!}{N_1! N_2!} \frac{N_2!}{v_1! v_2!} = \frac{N!}{N_1! v_1! v_2!} \quad (5.3-5)$$

We may now simply relabel the three containers as boxes 1, 2, and 3, and call the number of objects in each N_1 , N_2 , and N_3 , rather than N_1 , v_1 , and v_2 , in which case (5.3-5) may be written

$$Q(N_1, N_2, N_3) = \frac{N!}{N_1! N_2! N_3!} \quad (5.3-6)$$

Again, one may imagine the *third* compartment to be subdivided as before, and obtain in the same manner an expression for the number of ways of arranging N objects among four boxes so as to obtain a distribution (N_1, N_2, N_3, N_4) . By repeated application of this process, the result may be extended indefinitely by induction to cover the case where there may be n boxes. It is clear from the form of (5.3-3) and (5.3-6) that one will find

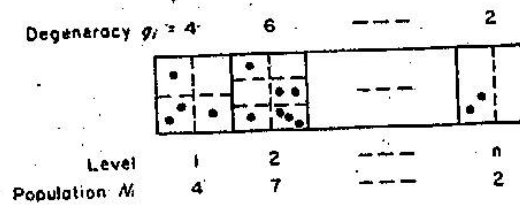
$$Q(N_1, N_2, N_3, \dots, N_n) = \frac{N!}{N_1! N_2! N_3! \dots N_n!} = \frac{N!}{\prod_{i=1}^n N_i!} \quad (5.3-7)$$

where the \prod notation is used to indicate an extended product in the same way that the more familiar \sum notation is used to express a summation.

The actual *probability* associated with a given distribution of N objects among n boxes is the number of independent ways of arranging objects among boxes $Q(N_1, \dots, N_n)$ which lead to that particular distribution, divided by the total number of ways of arranging N objects among n boxes *without regard for what distribution of objects among boxes results*. It is easily shown that this latter factor is simply n^N . The probability associated with a given distribution will then be $Q(N_1, \dots, N_n)/n^N$. We shall find it more convenient, however, to deal exclusively with the quantities $Q(N_1, \dots, N_n)$, which are *proportional* to the actual probabilities, since we shall only be interested in finding the values N_1, \dots, N_n which render the probability a maximum, and if $Q(N_1, \dots, N_n)$ is a maximum, then so is the associated probability.

Now let us identify the i th container with the i th energy level of the system and the number of objects N_i in that container with the number of particles belonging to that level. We must, however, allow for the fact that the energy levels may be degenerate, and we shall assume there are g_i independent quantum states associated with the i th energy level, each of which has the same *a priori* probability of being occupied, according to the fundamental postulate of Section 5.1. Each energy level must then be thought of not as a single container, but as a *group* of g_i containers, as illustrated in Figure 5.4. For a given energy level, say the i th, containing N_i particles and g_i

FIGURE 5.4. The subdivision of energy levels into separate quantum states according to their degeneracy. The separate quantum states play the role of the containers in the statistical development, each having equal statistical weight.



independent quantum states, there are $g_i^{N_i}$ ways of arranging the particles among the states or containers pertaining to that level, because there are g_i independent choices of where the first particle may be placed, and for *each* of these there are g_i choices of where the second may be placed, and so on to N_i factors. Each of these arrangements would constitute a separate statistically independent way of distributing particles among the quantum states of the system, since it is the quantum states themselves which are of equal probability, not the energy levels. If the first energy level, ϵ_1 , were the *only* degenerate level, then there would be $g_1^{N_1}$ times as many independent ways of forming a given distribution of particles among energy levels as is given by (5.3-7), because there are that many ways of permuting particles among separate degenerate states belonging to the first level, and for each of these there still remain the same number of ways of assigning particles to the other levels of the system in such a way that the distribution (N_1, N_2, \dots, N_n) results. If, in addition, the second level were degenerate, there would be $g_2^{N_2}$ possibilities for each one that existed before, the total number of independent ways of achieving a given distribution of particles among levels being now $g_1^{N_1} g_2^{N_2}$ times that given by (5.3-7). It is clear that when the degeneracy of all the levels is included, the result (5.3-7) will have to be multiplied by $g_1^{N_1} g_2^{N_2} g_3^{N_3} \dots g_n^{N_n}$, giving

$$Q(N_1, N_2, \dots, N_n) = \frac{N!}{\prod_{i=1}^n N_i!} \prod_{i=1}^n g_i^{N_i} \quad (5.3-8)$$

when degeneracy is included.

We shall now assume that the actual distribution (N_1, N_2, \dots, N_n) of particles among energy states which is observed in equilibrium is essentially that which can be realized in the *maximum* number of statistically independent ways, in other words, that for which the quantity Q of (5.3-8) is a maximum. Q must then be maximized with respect to the parameters N_1, N_2, \dots, N_n , subject to the restrictions

$$\sum_{i=1}^n N_i = N = \text{const.} \quad (5.3-9)$$

and

$$\sum_{i=1}^n \epsilon_i N_i = U = \text{const.} \quad (5.3-10)$$

This maximization is most easily carried out by the use of a mathematical technique called the method of Lagrangean multipliers, and we shall digress briefly to describe this subject. Suppose we are given a function $f(x_1, x_2, \dots, x_n)$ of n variables, and we are asked to find the values of x_1, x_2, \dots, x_n which make f a maximum under the restriction that some other given function $\phi(x_1, x_2, \dots, x_n)$ remain constant. For a maximum (or minimum) value of f , $df = 0$, and if ϕ remains constant, $d\phi = 0$, so that if f is a maximum or minimum under the stated conditions, then

$$df + \alpha d\phi = 0 \quad (5.3-11)$$

no matter what value the arbitrary undetermined multiplier α may have. But (5.3-11) may be written

$$\left(\frac{\partial f}{\partial x_1} + \alpha \frac{\partial \phi}{\partial x_1} \right) dx_1 + \left(\frac{\partial f}{\partial x_2} + \alpha \frac{\partial \phi}{\partial x_2} \right) dx_2 + \dots + \left(\frac{\partial f}{\partial x_n} + \alpha \frac{\partial \phi}{\partial x_n} \right) dx_n = 0. \quad (5.3-12)$$

According to this equation, condition (5.3-11) will certainly be fulfilled if for every i

$$\frac{\partial f}{\partial x_i} + \alpha \frac{\partial \phi}{\partial x_i} = 0 \quad (i = 1, 2, \dots, n), \quad (5.3-13)$$

while, in addition, we were given to begin with the fact that

$$\phi(x_1, x_2, \dots, x_n) = \text{const.} \quad (5.3-14)$$

Equations (5.3-13) and (5.3-14), taken together, represent a set of $n + 1$ simultaneous equations which can be solved for the n quantities x_1, x_2, \dots, x_n which maximize (or minimize) f and for the undetermined multiplier α which was introduced in (5.3-11).

If there are two auxiliary functions $\phi(x_1, x_2, \dots, x_n)$ and $\psi(x_1, x_2, \dots, x_n)$ which are to remain constant as the function f is maximized, then two arbitrary multipliers α and β are introduced and it is required that

$$df + \alpha d\phi + \beta d\psi = 0, \quad (5.3-15)$$

which leads, in the same manner, to a set of $n + 2$ equations

$$\frac{\partial f}{\partial x_i} + \alpha \frac{\partial \phi}{\partial x_i} + \beta \frac{\partial \psi}{\partial x_i} = 0 \quad (i = 1, 2, \dots, n) \quad (5.3-16)$$

$$\phi(x_1, x_2, \dots, x_n) = \phi_0 = \text{const.} \quad (5.3-17)$$

$$\psi(x_1, x_2, \dots, x_n) = \psi_0 = \text{const.} \quad (5.3-18)$$

for the $n + 2$ unknowns $x_1, x_2, \dots, x_n, \alpha$ and β .

We shall now proceed to apply this method to find the distribution N_1, N_2, \dots, N_n for which (5.3-8) is a maximum. As a matter of mathematical convenience, we shall actually maximize $\ln Q$ rather than Q itself, but since the logarithm is a single-valued monotonic function of all the variables involved, when $\ln Q$ is a maximum, so also is Q . If we take the logarithm of both sides of (5.3-8), we find

$$\ln Q(N_1, N_2, \dots, N_n) = \ln N! + \sum_{i=1}^n N_i \ln g_i - \sum_{i=1}^n \ln N_i! \quad (5.3-19)$$

We shall assume that our system is so large that for each level $N_i!$ may be approximated by Stirling's approximation, which states that for $x \gg 1$,

$$\ln x! \approx x \ln x - x. \quad (5.3-20)$$

Making use of this approximation, (5.3-19) becomes

$$\ln Q = \ln N! + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum_i N_i \quad (5.3-21)$$

which must be maximized under the restrictions

$$\phi(N_1, N_2, \dots, N_n) = \sum_i N_i = N \quad (5.3-22)$$

$$\psi(N_1, N_2, \dots, N_n) = \sum_i \epsilon_i N_i = U. \quad (5.3-23)$$

From (5.3-16), this requires that

$$\begin{aligned} \frac{\partial(\ln Q)}{\partial N_j} + \alpha \frac{\partial \phi}{\partial N_j} + \beta \frac{\partial \psi}{\partial N_j} &= \frac{\partial}{\partial N_j} \left[\sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum_i N_i \right] \\ &+ \alpha \frac{\partial}{\partial N_j} \left(\sum_i N_i \right) + \beta \frac{\partial}{\partial N_j} \left(\sum_i \epsilon_i N_i \right) = 0 \quad (j = 1, 2, \dots, n). \end{aligned} \quad (5.3-24)$$

Working out the derivatives in (5.3-24), noting that the only terms of the summations whose derivatives with respect to N_j are other than zero are those for which $i = j$, (5.3-24) can be reduced to

$$\ln g_j - \ln N_j + \alpha + \beta \epsilon_j = 0 \quad (j = 1, 2, \dots, n). \quad (5.3-25)$$

Solving for $\ln(N_j/g_j)$ and exponentiating, this can be rewritten in the form

$$\frac{N_j}{g_j} = e^{\alpha} e^{\beta \epsilon_j} = f(\epsilon_j). \quad (5.3-26)$$

Equation (5.3-26) gives the average number of particles per quantum state of the system and thus, by definition, represents the energy distribution function $f(\epsilon)$. This

particular energy distribution function obtained as (5.3-26) under the classical assumption of identifiable particles and without the use of the Pauli exclusion principle, is called the *Maxwell-Boltzmann* distribution function.

We must now discuss how the constants α and β are related to the physical properties of the system. To begin with, we shall assign to the constant β the value

$$\beta = -1/kT, \quad (5.3-27)$$

where T is the absolute temperature of the system and k is a constant called Boltzmann's constant, and we shall regard this equation, along with (5.3-26) as defining what is meant by temperature. We shall see, in due course, that this definition leads to all the familiar characteristics of temperature as related to an ideal gas, and it will then be clear that the definition of temperature could have been postponed until the properties of an ideal gas had been worked out from (5.3-26). An identification of β with the value given above could then have been assigned on the basis of a comparison of the results so obtained and the familiar thermodynamic equation of state for an ideal gas (from which the temperature is more commonly defined). It will be shown that the value of k can be related to the measured ideal gas constant R and Avogadro's number.

Using the value given by (5.3-27) for β , (5.23-6) may now be written

$$N_j = g_j e^{\alpha} e^{-\epsilon_j/kT}, \quad (5.3-28)$$

The value of the constant α may now be expressed in terms of the total number of particles N , since from (5.3-9) and (5.3-28)

$$N = \sum_j N_j = e^{\alpha} \sum_j g_j e^{-\epsilon_j/kT}, \quad (5.3-29)$$

whereby

$$e^{\alpha} = \frac{N}{\sum_j g_j e^{-\epsilon_j/kT}},$$

and

$$N_j = g_j e^{\alpha} e^{-\epsilon_j/kT} = \frac{N g_j e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}}$$

$$f(\epsilon_j) = \frac{N e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}} \quad (5.3-30)$$

$$f(\epsilon_j) = \frac{N e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}} \quad (5.3-31)$$

If the energy levels of the system are crowded very closely together, as are the levels of the gas of free particles which was discussed in the previous section, then the quantity g_j in (5.3-28) may be regarded as $g(\epsilon)d\epsilon$ and the quantity N_j in that equation may be regarded as $N(\epsilon)d\epsilon$, as discussed in connection with Equation (5.2-1). The number of particles in an energy range $d\epsilon$ about ϵ in this limit will, according to (5.3-28), be given by

$$N(\epsilon) d\epsilon = \left(e^{\alpha} e^{-\epsilon/kT} \right) g(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon. \quad (5.3-32)$$

For an ideal gas of free particles, the density of states factor $g(\epsilon)$ will be given by (5.2-22). Note that the form of (5.3-32) is the same as that of (5.2-1) with $f(\epsilon) = e^{\alpha} e^{-\epsilon/kT}$. Again, as discussed in connection with (5.3-31), we may evaluate the constant α by the condition that the total number of particles in the system shall be a constant N .

whereby

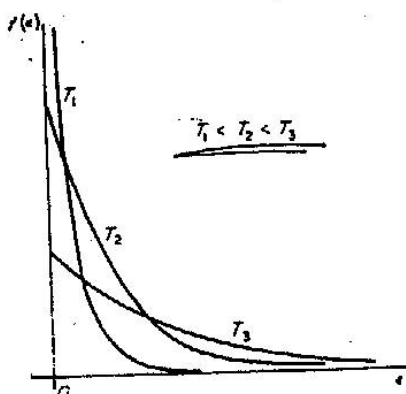
$$N = \int N(\epsilon) d\epsilon = e^{\alpha} \int g(\epsilon) e^{-\epsilon/kT} d\epsilon, \quad (5.3-33)$$

$$f(\epsilon) d\epsilon = \frac{N g(\epsilon) e^{-\epsilon/kT} d\epsilon}{\int g(\epsilon) e^{-\epsilon/kT} d\epsilon} \quad \text{and} \quad e^{\alpha} = \frac{N}{\int g(\epsilon) e^{-\epsilon/kT} d\epsilon} \quad (5.3-34)$$

the integrals being taken over all energies available to the particles of the system.

$$P(\epsilon) = \frac{N e^{-\epsilon/kT}}{\int g(\epsilon) e^{-\epsilon/kT} d\epsilon} = e^{\alpha} e^{-\epsilon/kT}$$

FIGURE 5.5. A schematic representation of the Maxwell-Boltzmann energy distribution function for three different temperatures.



We should note that the quantity Q of (5.3-8) is closely connected with the thermodynamic entropy of the system. At equilibrium, the state of the system is such that Q , the number of statistically independent ways of distributing particles among quantum states, is a maximum, as is the entropy of the system. We shall not go into details at this point, but it can indeed be demonstrated¹ that the relation between these two quantities is

$$S = k \ln Q, \quad (5.3-35)$$

where S is the entropy.

5.4 MAXWELL-BOLTZMANN STATISTICS OF AN IDEAL GAS

We shall now discuss the properties of an ideal gas of free particles of the type discussed in Section 4.2. For this system, the density of states factor $g(\epsilon) d\epsilon$ is given by (5.2-22), whereby, according to (5.3-34),

¹ J. E. Mayer and M. Göppert-Mayer, *Statistical Mechanics*, John Wiley and Sons, New York (1940), Chapter 4.

OUTLINE OF STATISTICAL MECHANICS

$$e^{\epsilon} = \frac{N}{8\sqrt{2\pi V m^{3/2}} h^3} \int_0^{\infty} \epsilon e^{-\epsilon/kT} d\epsilon$$

$$\begin{aligned} & \int_0^{\infty} \epsilon e^{-\epsilon/kT} d\epsilon \\ &= \int_0^{\infty} \epsilon e^{-x} \frac{dx}{kT} \\ &= \frac{1}{kT} \int_0^{\infty} \epsilon e^{-x} dx \quad (5.4-1) \\ &= \frac{1}{kT} \times k^2 T^2 \end{aligned}$$

The integration is taken between the limits zero and infinity, since the energy of the particles is entirely kinetic, hence positive. The integral in (5.4-1) may be expressed in a simpler form by the substitution

$$x = \epsilon/kT, \quad kT dx = d\epsilon$$

whence (5.4-1) becomes

$$e^{\epsilon} = \frac{N}{8\sqrt{2\pi V} \left(\frac{mkT}{h^2}\right)^{3/2}} \int_0^{\infty} x^{1/2} e^{-x} dx$$

$$\frac{N}{k^{3/2} T^{3/2}} \int_0^{\infty} x^{1/2} e^{-x} dx \quad (5.4-3)$$

The integral can now be expressed as a Γ -function,² since $\Gamma(n)$ is defined as

$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x} dx, \quad \Gamma\left(\frac{3}{2}\right) \quad (5.4-4)$$

the integral in (5.4-3) thus being equal to $\Gamma(3/2)$, which in turn equals $\sqrt{\pi}/2$. Inserting this value into (5.4-3), we find

$$e^{\epsilon} = \frac{N}{2V} \left(\frac{h^2}{2\pi mkT}\right)^{3/2} \quad (5.4-5)$$

which makes it possible to write the Maxwell-Boltzmann distribution function for an ideal gas as

$$f(\epsilon) = e^{\epsilon} e^{-\epsilon/kT} = \frac{N}{2V} \left(\frac{h^2}{2\pi mkT}\right)^{3/2} e^{-\epsilon/kT} \quad (5.4-6)$$

It will be noted that the value of e^{ϵ} given by (5.4-5) is temperature dependent. It should also be emphasized that this particular value for e^{ϵ} pertains only to the free particle density of states function (5.2-22) and that for systems having other density of states functions associated with them the value for e^{ϵ} will be different from that given by (5.4-5). A plot of the Boltzmann distribution (5.4-6) for several temperatures is shown in Figure 5.5. From (5.4-6) and (5.2-22) it is clear that the actual distribution of particle density with energy is given by

$$N(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (5.4-7)$$

² See, for instance, I. S. and E. S. Sokolnikoff, *Higher Mathematics for Engineers and Physicists*, McGraw-Hill Book Co., Inc., New York (1941), pp. 273-276.

The total internal energy and specific heat of the gas can be obtained very easily from these results. Since the energy of the particles in the range de about ϵ is simply $\epsilon N(\epsilon) d\epsilon$, the total internal energy of the gas is

$$U = \int_0^{\infty} \epsilon N(\epsilon) d\epsilon, \quad (5.4-8)$$

or, using (5.4-7),

$$U = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon. \quad (5.4-9)$$

This integral can be evaluated in terms of Γ -functions by making the substitution (5.4-2). Working out the integral in this way, noting that $\Gamma(5/2) = (3/2)\Gamma(3/2) = 3\sqrt{\pi}/4$, we find

$$U = \frac{3}{2} NkT, \quad (5.4-10)$$

whence the average internal energy per particle, U/N , is $\frac{3}{2}kT$, an important and familiar result. The heat capacity of the gas at constant volume is the rate of increase of internal energy with respect to temperature, whereby from (5.4-10),

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{3}{2} Nk, \quad (5.4-11)$$

independent of temperature. The specific heat c_v is simply the heat capacity per unit volume.

Our objective, eventually, is to derive the equation of state for an ideal Boltzmann gas from the dynamical properties of the particles and from the distribution function. Before doing this, however, we must convert the *energy* distributions (5.4-6) and (5.4-7) into appropriate velocity distributions, and investigate briefly how to use these velocity distribution functions. Table 5.1 gives the value of some of the definite integrals which are frequently encountered when working with the Boltzmann velocity distributions.

In a gas of free particles possessing no internal degrees of freedom, all the energy resides in the kinetic energy of the particles. We may relate this to the velocity by writing

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \quad (5.4-12)$$

whence

$$d\epsilon = mv dv, \quad (5.4-13)$$

and the energy distribution (5.4-7) may be written directly as a velocity distribution of the form

$$\left(N(v) dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \right) \quad (5.4-14)$$

This function expresses the number of particles of the system whose speeds lie in a range dv about v , or the number of particles which lie within a spherical shell of thickness dv and radius v in velocity space.

TABLE 5.1.
Maxwell-Boltzmann Integrals*

$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2} \sqrt{\frac{2\pi kT}{m}} = \frac{\pi \bar{c}}{4}$
$\int_0^\infty x e^{-\alpha x^2} dx = \frac{1}{2\alpha} = \frac{kT}{m} = \frac{\pi \bar{c}^2}{8}$
$\int_0^\infty x^3 e^{-\alpha x^2} dx = \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{\sqrt{\pi}}{4} \left(\frac{2kT}{m} \right)^{3/2} = \frac{\pi^2 \bar{c}^3}{32}$
$\int_0^\infty x^5 e^{-\alpha x^2} dx = \frac{1}{2\alpha^2} = \frac{1}{2} \left(\frac{2kT}{m} \right)^2 = \frac{\pi^2 \bar{c}^4}{32}$
$\int_0^\infty x^7 e^{-\alpha x^2} dx = \frac{3}{8\alpha^2} \sqrt{\frac{\pi}{\alpha}} = \frac{3\sqrt{\pi}}{8} \left(\frac{2kT}{m} \right)^{5/2} = \frac{3\pi^3 \bar{c}^5}{256}$
$\int_0^\infty x^9 e^{-\alpha x^2} dx = \frac{1}{\alpha^3} = \left(\frac{2kT}{m} \right)^3 = \frac{\pi^3 \bar{c}^6}{64}$
$\int_0^\infty x^{11} e^{-\alpha x^2} dx = \frac{15}{16\alpha^3} \sqrt{\frac{\pi}{\alpha}} = \frac{15\sqrt{\pi}}{16} \left(\frac{2kT}{m} \right)^{7/2} = \frac{15\pi^4 \bar{c}^7}{2^{11}}$
$\int_0^\infty x^{13} e^{-\alpha x^2} dx = \frac{3}{\alpha^4} = 3 \left(\frac{2kT}{m} \right)^4 = \frac{3\pi^4 \bar{c}^8}{256}$
$\int_0^\infty x^{15} e^{-\alpha x^2} dx = \frac{105}{32\alpha^4} \sqrt{\frac{\pi}{\alpha}} = \frac{105\sqrt{\pi}}{32} \left(\frac{2kT}{m} \right)^{9/2} = \frac{105\pi^5 \bar{c}^9}{2^{14}}$

* The second column in the table gives the value of the definite integral shown in the first column. The third column gives the value of the definite integral when α is set equal to $m/2kT$, which is usually the case when working with Boltzmann velocity distributions. The fourth column expresses the result shown in the third column as a multiple of the mean thermal speed \bar{c} , where

$$\bar{c} = \sqrt{8kT/\pi m}.$$

Suppose now that we wish to know how many particles of the system have velocities such that the x -component of velocity is in a range dv_x about v_x , the y -component is in a range dv_y about v_y , and the z -component is in a range dv_z about v_z , thus the number of particles in a rectangular volume element $(dv_x dv_y dv_z)$ in velocity space centered on the value (v_x, v_y, v_z) . We shall call this number $N(v_x, v_y, v_z) dv_x dv_y dv_z$. We must now proceed more carefully, starting with (5.4-6), which according to (5.4-12) we may write as

$$f(v_x, v_y, v_z) = \frac{N}{2V} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT}. \quad (5.4-15)$$

Then, as required by (5.2-1),

$$N(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x, v_y, v_z) g(v_x, v_y, v_z) dv_x dv_y dv_z. \quad (5.4-16)$$

where $g(v_x, v_y, v_z) dv_x dv_y dv_z$ is the number of quantum states within the velocity space element $dv_x dv_y dv_z$. From (5.2-17) the number of states in a volume element $dp_x dp_y dp_z$ of momentum space is $(2V/h^3)(dp_x dp_y dp_z)$, whereby

$$\frac{2V}{h^3} dp_x dp_y dp_z = \frac{2m^3 V}{h^3} dv_x dv_y dv_z = g(v_x, v_y, v_z) dv_x dv_y dv_z. \quad (5.4-17)$$

Since the density of states in momentum space is constant, so also is the density of states in velocity space. Substituting (5.4-15) and (5.4-17) into (5.4-16) and simplifying, we find

$$N(v_x, v_y, v_z) dv_x dv_y dv_z = N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} dv_x dv_y dv_z. \quad (5.4-18)$$

A third velocity distribution function, $N(v_x)dv_x$, representing the number of particles whose x -component of velocity lies in a range dv_x about v_x , regardless of what values the y - and z -components of velocity for those particles may have, is closely related to the distribution function (5.4-18). The distribution function $N(v_x)dv_x$ can be calculated from (5.4-18) by integrating over all possible values of v_y and v_z , the result being

$$N(v_x)dv_x = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [N(v_x, v_y, v_z) dv_y dv_z] dv_x = N \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} dv_x. \quad (5.4-19)$$

The values of the definite integrals required in integrating (5.4-18) have been taken from Table 5.1. A plot of the distributions $N(v)$ and $N(v_x)$ as functions of the appropriate velocity coordinate is shown in Figure 5.6.

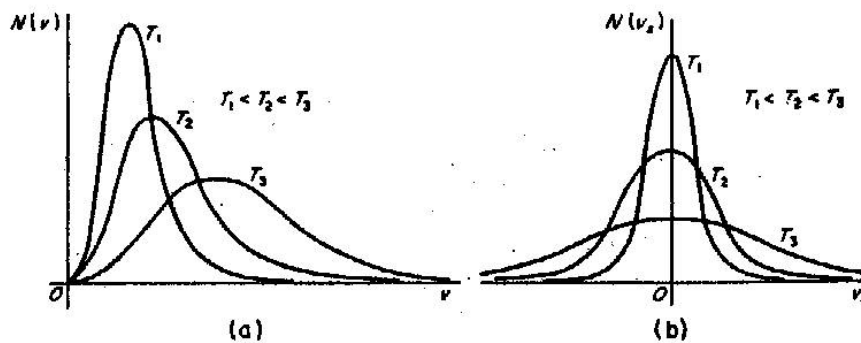


FIGURE 5.6. (a) A schematic representation of the Maxwell-Boltzmann distribution of particle speeds, $N(v)$, for three different temperatures. (b) The corresponding distribution of x -components of velocity, $N(v_x)$.

Knowing these three velocity distribution functions it is an easy matter to evaluate averages over the velocity distributions. For example, the average thermal speed \bar{v}

for a particle in a Boltzmann distribution is obtained quite simply from (5.4-14) by writing

$$\begin{aligned} \overline{v} &= \frac{\int_0^\infty v N(v) dv}{\int_0^\infty N(v) dv} = \frac{1}{N} \cdot 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT} dv \\ &= \sqrt{8kT/\pi m}, \end{aligned} \quad (5.4-20)$$

the integral having been evaluated with the help of Table 5.1.

We are now in a position to discuss the equation of state of an ideal gas. Consider the particles striking unit area of the wall of a container filled with such a gas, as shown in Figure 5.7. If the wall is a plane oriented normal to the x -axis, the momentum components p_x and p_z of the particles striking the wall are conserved if the collisions of the

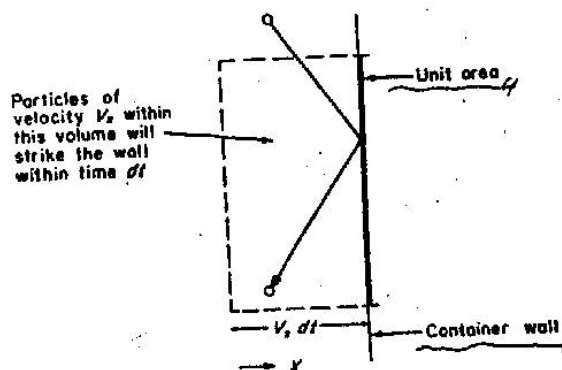


FIGURE 5.7. The elastic collision of a particle whose x -component of velocity is v_x with the wall of a rigid, fixed container.

particles with the walls are elastic, which we shall assume to be the case. In each collision the velocity component v_x directed toward the wall is changed to $-v_x$, directed away from the wall. The transfer of momentum from the particle to the wall, per collision, is thus $2mv_x$. The transfer of momentum to the wall in time dt is this quantity times the number of particles which collide with the wall during that time; for particles whose x -component of velocity is v_x , this is simply the number of such particles in a volume extending a distance $d = v_x dt$ behind the wall, or the number per unit volume times $v_x dt$, thus $v_x dt \cdot N(v_x) dv_x / V$. The momentum transfer in time dt for particles of velocity in the range dv_x about v_x is then

$$(dp_x)_{v_x} = 2mv_x \cdot v_x dt \cdot \frac{N(v_x) dv_x}{V}$$

or,

$$\left[\frac{dp_x}{dt} \right]_{v_x} = \frac{2m}{V} v_x^2 N(v_x) dv_x \quad (5.4-21)$$

The total rate of momentum transfer to the walls by collisions involving particles with all possible values of v_x can be obtained by integrating over v_x , giving, with the help of (5.4-19) and Table 5.1,

$$\frac{dp_x}{dt} = \frac{2m}{V} N \sqrt{\frac{m}{2\pi kT}} \int_0^\infty v_x^2 e^{-mv_x^2/2kT} dv_x = \frac{NkT}{V}. \quad (5.4-22)$$

The time rate of transfer of momentum to unit area of the container wall, however, is according to Newton's law equal to the force experienced by a unit area of the wall, which by definition is the pressure P . Equation (5.4-22) then reduces to

$$PV = NkT, \quad (5.4-23)$$

which is the equation of state for a Boltzmann gas of independent particles.

This equation has the form of the familiar ideal gas law, which is more commonly written in the form

$$PV = nRT, \quad (5.4-24)$$

where n is the number of moles of gas in the system and R is an experimentally measured "molar gas constant" which is the same for all "ideal" gases. If there are n moles of gas present, then the number of particles must be given by $N = nN_A$, where N_A is Avogadro's number, equal to 6.026×10^{23} molecules per mole. Under these conditions (5.4-23) takes the form

$$PV = nN_A kT, \quad (5.4-25)$$

whence, comparing (5.4-24) with (5.4-25), it is clear that Boltzmann's constant k must be given by

$$k = R/N_A. \quad (5.4-26)$$

Boltzmann's constant is thus simply the gas constant per particle of the system. Its value can be derived from N_A and R , and is equal to 1.380×10^{-16} ergs/°K, or 8.615×10^{-5} eV/°K.

It is clear now that the value for the constant β in the distribution function which was assumed in (5.3-27) was chosen correctly. Had we carried through all our calculations up to this point without ever having assumed any value for β , we should have found for equation (5.4-23), instead,

$$PV = -N/\beta, \quad (5.4-27)$$

and in order that our results be in agreement with the experimentally established gas law (5.4-24) we should have been forced to choose

$$\begin{aligned} -N/\beta &= nRT = \frac{N}{N_A} RT, \\ \text{or,} \quad \beta &= -\frac{N_A}{RT} = -1/kT. \end{aligned} \quad (5.4-28)$$

5.5 FERMİ-DİRAC STATISTICS

In the development of the Maxwell-Boltzmann distribution function, the particles are considered to be distinguishable, while in actual fact it is quite impossible to distinguish one electron or other elementary particle from another. Furthermore, we permitted any number of particles to occupy the same quantum state of the system, in spite of the fact that many particles, *electrons* in particular, obey the Pauli exclusion principle, which allows each quantum state to accept no more than one particle. If these additional conditions are imposed upon the system, the calculations of Section 5.4 must be modified, resulting in another distribution function, which is called the Fermi-Dirac distribution function. This energy distribution is of the greatest importance, since it describes the statistical behavior of free electrons in metals and semiconductors, and since many of the electrical and thermal properties of solids which could not be understood at all on the basis of classical statistics follow as a direct consequence of the Fermi-Dirac statistics.

If the particles of the system are indistinguishable, they cannot be identified by number in the manner which was adopted when discussing the various possibilities illustrated in Figure 5.2. As a matter of fact, all the various distributions in each row of Figure 5.2 leading to $Q(N_1, N_2)$ for a particular value of N_1 are the same if the numbered labels are removed from the particles, in which case the factor (5.3-7) reduces to unity. It is still possible, however, to permute the N_1 particles in the i th energy level among the g_i quantum states belonging to that level in many ways, each of which constitutes a statistically independent way of achieving an arrangement wherein N_i particles are in the i th energy level of the system, as shown in Figure 5.8. The product

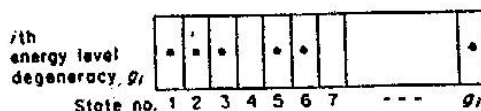


FIGURE 5.8. A possible distribution of particles among quantum states in the i th energy level of a system wherein the Pauli exclusion principle is applicable.

of the possible numbers of permutations of particles among quantum states over all energy levels of the system then gives the number of independent ways of realizing a given distribution of particles among energy levels.

For the Fermi-Dirac case, in which the Pauli exclusion principle is assumed to apply, a maximum of one particle per quantum state is allowed. Referring to Figure 5.8, which depicts the i th energy level of the system, there are g_i ways of choosing where to insert a first particle, $g_i - 1$ ways of choosing where to insert a second, since the second cannot occupy the same quantum state as the first, $g_i - 2$ ways of choosing where to insert a third, and so forth. The total number of ways of arranging N_i particles in the i th level obtained on this basis is

$$g_i(g_i - 1)(g_i - 2) \cdots (g_i - N_i + 1) = \frac{g_i!}{(g_i - N_i)!} \quad (5.5-1)$$

However, since the particles are indistinguishable, the $N_i!$ ways of permuting the

particles among themselves in any given arrangement of particles among states do not count as separate arrangements. The actual number of independent ways of realizing a distribution of N_i particles in the i th level is thus arrived at by dividing (5.5-1) by $N_i!$, giving

$$\frac{g_i!}{N_i!(g_i - N_i)!} \quad (5.5-2)$$

The total number of independent ways of realizing a distribution of (N_1, N_2, \dots, N_n) indistinguishable particles among n energy levels, no more than one per quantum state, is just the product of individual factors of the form (5.5-2) over all the levels, that is,

$$Q_f(N_1, N_2, \dots, N_n) = \prod_{i=1}^n \frac{g_i!}{N_i!(g_i - N_i)!} \quad (5.5-3)$$

We now proceed to maximize the logarithm of this quantity with respect to the variables N_1, N_2, \dots, N_n by the method of Lagrangean multipliers used in Section 5.3. We find from (5.5-3) that

$$\ln Q_f = \sum_i \ln g_i! - \sum_i \ln N_i! - \sum_i \ln(g_i - N_i)!, \quad (5.5-4)$$

which by using Stirling's approximation (5.3-20) can be written

$$\ln Q_f = \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln(g_i - N_i)]. \quad (5.5-5)$$

$\ln x! = x \ln x - x$

Again, it is required that the total number of particles in the system and the total energy of the system be constant, which means that Equations (5.3-22) and (5.3-23) must hold here also, in which case one may write, as before,

$$\frac{\partial(\ln Q_f)}{\partial N_j} + \alpha \frac{\partial \phi}{\partial N_j} + \beta \frac{\partial \psi}{\partial N_j} = 0 \quad (j = 1, 2, \dots, n), \quad (5.5-6)$$

where ϕ and ψ are given by (5.3-22) and (5.3-23). Substituting (5.5-5), (5.3-22), and (5.3-23) into this equation, one obtains

$$-\frac{\partial}{\partial N_j} \left[\sum_i N_i \ln N_i + \sum_i (g_i - N_i) \ln(g_i - N_i) \right] + \alpha \frac{\partial}{\partial N_j} \left(\sum_i N_i \right) + \beta \frac{\partial}{\partial N_j} \left(\sum_i \epsilon_i N_i \right) = 0. \quad (5.5-7)$$

Working out the derivatives as in Section 5.3, we find

$$\ln(g_j - N_j) - \ln N_j = -\alpha - \beta \epsilon_j, \quad (5.5-8)$$

or, rearranging, exponentializing and solving for $N_j/g_j = f(\epsilon_j)$,

$$f(\epsilon_j) = N_j/g_j = \frac{1}{1 + e^{-\alpha - \beta \epsilon_j}}. \quad (5.5-9)$$

$$\frac{g_j - N_j}{N_j} = -\alpha - \beta \epsilon_j$$

$$\ln \left(\frac{g_j}{N_j} - 1 \right) = -\alpha - \beta \epsilon_j$$

$$\frac{g_j}{N_j} - 1 = e^{-\alpha - \beta \epsilon_j}$$

$$\frac{g_j}{N_j} = 1 + e^{-\alpha - \beta \epsilon_j}$$

$$\frac{N_j}{g_j} = \frac{1}{1 + e^{-\alpha - \beta \epsilon_j}}$$

This is the Fermi-Dirac distribution function.

As in Section 5.4, we shall take the value of β to be

$$\beta = -1/kT, \quad (5.5-10)$$

postponing until later the justification for this step. It is customary to write α in the form

$$\alpha = \epsilon_f/kT, \quad (5.5-11)$$

where ϵ_f is a parameter with the dimensions of energy, which is called the Fermi energy, or the Fermi level, of the system. Equation (5.5-9) then becomes

$$N_j = \frac{g_j}{1 + e^{(\epsilon_j - \epsilon_f)/kT}}, \quad (5.5-12)$$

or, if the levels are assumed to crowd together into a continuum, so that $g_j(\epsilon_j) \rightarrow g(\epsilon)d\epsilon$, then

$$N(\epsilon)d\epsilon = g(\epsilon)f(\epsilon)d\epsilon = \frac{g(\epsilon)d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}}. \quad (5.5-13)$$

For a gas of independent particles such as free electrons, $g(\epsilon)d\epsilon$ is represented by (5.2-22), just as for a Maxwell-Boltzmann gas.

The Fermi energy ϵ_f is in general a function of the temperature, whose form and temperature dependence are critically dependent upon the density of states function for the system, just as for the corresponding parameter e^a of the Maxwell-Boltzmann distribution. Its value is determined by the condition (5.3-22), or for a continuum of levels, by

$$N = \text{const.} = \int \frac{g(\epsilon)d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}} = \int g(\epsilon)f(\epsilon)d\epsilon. \quad (5.5-14)$$

The integral is taken over all energies available to the particles of the system. For a Fermi gas of independent particles, $g(\epsilon)$ is given by (5.2-22) and ϵ_f is determined by

$$N = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{\epsilon} d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}}. \quad (5.5-15)$$

Unfortunately, this integral cannot be evaluated in closed analytic form, so that ϵ_f cannot be determined as a simple function of the temperature. For a two-dimensional independent particle gas, however, the density of states function can be shown by the methods used to derive (5.2-22) to be

$$g(\epsilon)d\epsilon = \frac{4\pi mA}{h^2} d\epsilon, \quad (5.5-16)$$

independent of energy (Exercise 3, Chapter 5). In this formula, A represents the

area of the two-dimensional "container." For this system (5.5-14) becomes

$$N = \frac{4\pi mA}{h^2} \int_0^\infty \frac{d\varepsilon}{1 + e^{(\varepsilon - \varepsilon_f)/kT}}, \quad (5.5-17)$$

which can be evaluated in closed form, allowing one to solve for ε_f and obtain

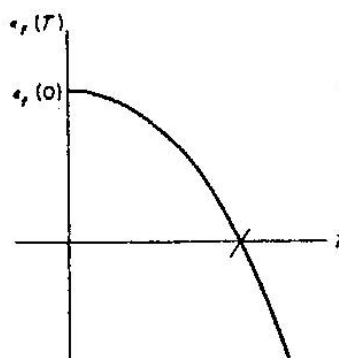
$$\varepsilon_f(T) = kT \ln(e^{\varepsilon_f(0)/kT} - 1), \quad (5.5-18)$$

where

$$\varepsilon_f(0) = \frac{Nh^2}{4\pi mA} \quad (5.5-19)$$

is the value which $\varepsilon_f(T)$ as given by (5.5-18) assumes as T approaches zero. The details of calculating this result are very instructive, and are assigned as an exercise for the reader. The variation of the Fermi energy of the two-dimensional independent particle gas with temperature is shown in Figure 5.9. It will be noted for this case that the Fermi energy is a monotonic decreasing function of temperature. (The Fermi energy for the three-dimensional Fermi gas, with the density of states function (5.2-22) will be found to exhibit the same general behavior, except that in this case the variation of the Fermi energy with temperature is linear with temperature at reasonably low temperatures, while for the two-dimensional example the variation is much more complex at low temperatures. (For many systems, including these two, the variation of the Fermi level with temperature is quite small over the range of physically realizable temperatures; in Figure 5.9 the temperature for which $\varepsilon_f = 0$ would be of the order of

FIGURE 5.9. Schematic representation of the variation of Fermi energy with temperature in a two-dimensional free electron gas, according to (5.5-18).



75 000°K for an electron gas with the free-electron density of metallic copper. For this reason, in many applications the temperature dependence of the Fermi energy may either be neglected or approximated by a linear or other appropriate function of temperature.

The Fermi distribution function itself,

$$f(\varepsilon) = \frac{1}{1 + e^{(\varepsilon - \varepsilon_f)/kT}}, \quad (5.5-20)$$

is plotted in Figure 5.10 for several values of the temperature. Since only one particle

may occupy a given quantum state, the value of $f(\epsilon)$ for a Fermi distribution at a particular energy is just equal to the probability that a quantum state of that energy will be occupied. At absolute zero, it is easily seen from Figure 5.10 and from (5.5-20) that the Fermi distribution function becomes simply the step function

$$\begin{aligned} f(\epsilon) &= 1 & (\epsilon < \epsilon_f) \\ &= 0 & (\epsilon > \epsilon_f). \end{aligned} \quad (5.5-21)$$

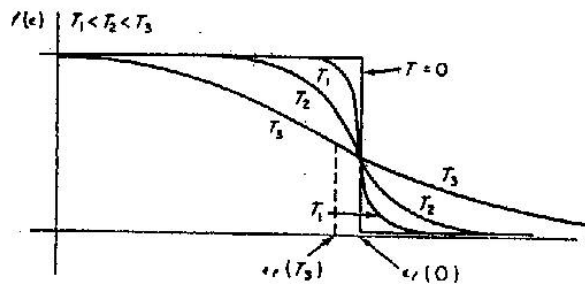


FIGURE 5.10. Schematic representation of the Fermi distribution function for four different temperatures. Note the variation of the Fermi energy with temperature. The temperature dependence of the Fermi energy depicted here is typical of a three-dimensional free-electron gas, but the actual variation in any particular system will depend critically upon the density of states function (or level degeneracies) for that system.

As the temperature increases, the edges of the step are rounded off, and the distribution function varies rapidly from nearly unity to nearly zero over an energy range of a few times kT around the value $\epsilon = \epsilon_f$. (At the same time, the value of ϵ_f itself changes, the variation illustrated in Figure 5.10 being approximately that associated with the three-dimensional electron gas whose density of states is given by (5.2-22). At very high temperatures, the distribution function loses its step-like character and varies much more slowly with energy. From (5.5-20), it is clear that the value of $f(\epsilon)$ at $\epsilon = \epsilon_f$ is just $\frac{1}{2}$, that is,

$$f(\epsilon_f) = \frac{1}{2}, \quad (5.5-22)$$

hence a quantum state at the Fermi level has a probability of occupation of $\frac{1}{2}$.

Figure 5.11 shows the actual distribution of particle density $N(\epsilon)$ as a function of energy for a Fermi gas of independent particles, as given by (5.5-13) with the density of states function (5.2-22). Again, at $T = 0$ the curve has a step-like character, the portion for which $(\epsilon < \epsilon_f)$ being the density of states parabola (5.2-22) and that for which $(\epsilon > \epsilon_f)$ being zero. As the temperature increases this step-like aspect becomes less and less pronounced, as shown in the drawing. At low temperatures, when the Fermi distribution function is step-like, the distribution is said to be highly degenerate.

At low temperatures, the Fermi-Dirac distribution may be represented as a sphere in momentum space in which all or most of the quantum states of energy less than ϵ_f

are filled, while all or most of the states of energy greater than ϵ_f are empty. From (5.2-14), the equation of the surface of this "Fermi sphere" must be

$$p_x^2 + p_y^2 + p_z^2 = 2m\epsilon_f, \quad (5.5-23)$$

the radius therefore being $\sqrt{2m\epsilon_f}$, as shown in Figure 5.12. At very high temperatures the surface of the Fermi sphere becomes poorly defined, due to the disappearance of the step-like aspect of $f(\epsilon)$, and the concept loses some of its usefulness.

FIGURE 5.11. Schematic representation of electron density as a function of energy for a three-dimensional free-electron gas.

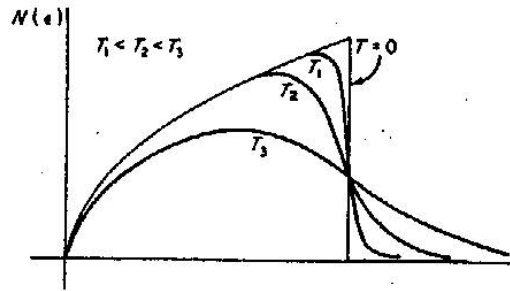
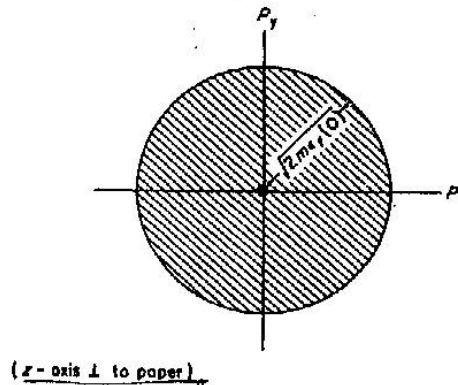


FIGURE 5.12. The representation of the absolute zero Fermi distribution for a free-electron gas as a sphere of electrons in momentum space. This representation is a useful one so long as $T \ll T_F$.



Although, as we have already seen, the fact that the integral (5.5-15) cannot be evaluated in closed form prevents us from finding a simple expression for the Fermi energy of a three-dimensional Fermi gas at all temperatures, the simple character (5.5-21) which the function assumes at $T = 0$ permits one to evaluate ϵ_f very simply at absolute zero. Using (5.5-21) to represent $f(\epsilon)$ at $T = 0$, we may rewrite (5.5-14), using the density of states function (5.2-22), as

$$\left(\frac{N}{V} = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \int_0^{\epsilon_f(0)} \sqrt{\epsilon} d\epsilon = \frac{16\sqrt{2}\pi m^{3/2} [\epsilon_f(0)]^{3/2}}{3h^3} \right) \quad (5.5-24)$$

Solving this equation for $\epsilon_f(0)$, we may obtain

$$\left(\epsilon_f(0) = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \right) \quad (5.5-25)$$

In a somewhat similar manner, it is possible to obtain the internal energy of a Fermi gas at absolute zero, the result being

$$\frac{U_0}{V} = \frac{\pi h^2}{40m} \left(\frac{3N}{\pi V} \right)^{5/3} = \frac{3}{5} \frac{N}{V} \epsilon_f(0). \quad (5.5-26) \quad \checkmark$$

The details of this calculation are assigned as an exercise.

For energies which are much greater than ϵ_f , $e^{(\epsilon - \epsilon_f)/kT}$ is much larger than unity and for such energies the Fermi-Dirac distribution function (5.5-20) may be written approximately as

$$f(\epsilon) \approx e^{\epsilon_f/kT} e^{-\epsilon/kT}. \quad (5.5-27)$$

If all the energies available to the system satisfy the condition

$$\epsilon - \epsilon_f \gg kT, \quad (5.5-28)$$

that is, if ϵ_f is many kT units smaller than any energy a particle belonging to the system may have, then (5.5-27) will be a good approximation to (5.5-20) for all particles of the system. The approximate distribution function (5.5-27), however, is simply the Maxwell-Boltzmann distribution function of (5.4-6) with $\alpha = \epsilon_f/kT$. If the condition (5.5-28) holds, then, for all particles of the system, the Fermi-Dirac distribution and the Maxwell-Boltzmann distribution are very nearly the same.

For the two-dimensional Fermi gas, where the Fermi energy is given by (5.5-18), if T is so large that $kT \gg \epsilon_f(0)$, the exponent $\epsilon_f(0)/kT$ will be small, so that the exponential can be approximated by $1 + [\epsilon_f(0)/kT]$, giving

$$\begin{aligned} \epsilon_f(T) &= kT \ln \frac{\epsilon_f(0)}{kT} \\ &= \epsilon_f(0) \left[\frac{kT}{\epsilon_f(0)} \ln \frac{\epsilon_f(0)}{kT} \right] \\ &= -\epsilon_f(0) \left[\frac{kT}{\epsilon_f(0)} \ln \frac{kT}{\epsilon_f(0)} \right]. \end{aligned} \quad (5.5-29)$$

From this, we see that as T becomes large, $\epsilon_f(T) \rightarrow -\infty$. Since the lowest energy any particle of the system may have is zero, it is clear that condition (5.5-28) will be fulfilled for sufficiently high temperatures, and the distribution function will therefore be approximately the same as the Maxwell-Boltzmann distribution at very high temperatures. The same result can be shown to hold for the three-dimensional case. These results are to be expected on physical grounds, since at high temperatures the particles are distributed over a very wide range of energy states, the number of particles in every range of available energies being so small that there are always many more available quantum states than there are particles to occupy them. Under these circumstances, the probability of two or more particles occupying the same quantum state becomes vanishingly small in any case, so that there is not much difference

between the distribution function for which the Pauli principle is obeyed (the Fermi-Dirac distribution) and that for which it is not (the Maxwell-Boltzmann distribution).³ Since the quantity $\epsilon_f(0)$ which is required to be much less than kT for the two distributions to coincide is proportional to the density of particles N/V by (5.5-19), the reduction of the Fermi distribution to a Maxwell-Boltzmann distribution will take place at lower temperatures in less dense gases. By the same token, according to (5.5-19) it will take place at lower temperatures in gases where the particle mass m is large. It is for these reasons that ordinary gaseous substances obey the Maxwell-Boltzmann statistics at normal temperatures rather than the Fermi-Dirac (or Bose-Einstein) statistics. For a dense gas of very light particles, such as the free electrons in a metal, however, the Fermi energy at absolute zero is quite large, and the condition (5.5-28) can be satisfied for all particles of the system only at temperatures so high as to be unrealizable physically. A dense free electron gas must therefore be treated using Fermi-Dirac statistics. In semiconductors, however, the peculiar form of the density of states function is such that the Maxwell-Boltzmann distribution is virtually *always* a good approximation to the Fermi-Dirac distribution. We shall examine this situation in considerable detail in a later chapter.

Had we made a choice for the undetermined multiplier β other than that given by (5.5-10) we should *not* in general have found the correspondence between the Fermi-Dirac and Maxwell-Boltzmann systems in the high-temperature limit, which, as we have seen, we have every right to expect on physical grounds. We must therefore conclude that the value for β as given by (5.5-10) is physically justified.

5.6 THE BOSE-EINSTEIN DISTRIBUTION

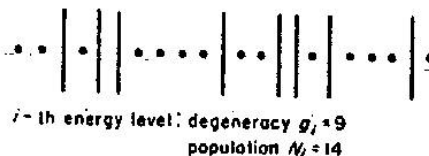
In the previous section we showed that the statistical distribution which characterizes the behavior of an ensemble of indistinguishable particles which obey the Pauli exclusion principle is the Fermi-Dirac distribution (5.5-20). Since not all elementary particles obey the Pauli principle (photons being the most conspicuous exception) it is necessary to consider the statistical behavior of particles which, though indistinguishable, do not obey the Pauli exclusion principle. In this case again, since the particles are not numbered, the factor (5.3-7) reduces to unity and we need only consider the possible permutations of N_i identical particles among the g_i quantum states of the i th energy level, but now with no restrictions with regard to the number of particles which may occupy any given quantum state.

Consider a linear array of N_i particles and $g_i - 1$ partitions which would be necessary to divide these particles into g_i groups, as shown in Figure 5.13. It is not difficult to see that the number of ways of permuting the N_i particles among g_i levels is equal to the number of independent permutations of objects and partitions in Figure 5.13.

³ It might be contended that the indistinguishability of particles renders the Fermi-Dirac distribution distinct from the Maxwell-Boltzmann distribution even in this limit. It can, however, be shown, as we shall see in the next section, that the distribution function for *indistinguishable* particles which do not obey the Pauli exclusion principle (the Bose-Einstein distribution) also approaches the Maxwell-Boltzmann distribution function in this limit. A more accurate way of explaining the situation would be to say that in the high-temperature limit the Fermi-Dirac distribution approaches the Bose-Einstein distribution, which in turn approaches the Maxwell-Boltzmann distribution.

Since there are a total of $N_i + g_i - 1$ particles plus partitions, these can be arranged linearly in $(N_i + g_i - 1)!$ ways, but since permutations of particles among themselves or of partitions among themselves do not count as independent arrangements, we must divide by the number of ways of permuting particles among themselves ($N_i!$)

FIGURE 5.13. A possible distribution of particles among quantum states in the i th energy level of a system to which the Pauli exclusion principle does not apply.



and again by the number of ways of permuting partitions among themselves $((g_i - 1)!)$, giving

$$\frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \quad (5.6-1)$$

ways of realizing a distribution of $N_i!$ indistinguishable particles among g_i states which may accommodate any number of particles. The number Q_b of statistically independent ways of achieving a distribution (N_1, N_2, \dots, N_n) particles among the energy levels of the system according to these rules is then just the product of factors of the form (5.6-1) over all levels of the system, whence

$$Q_b(N_1, N_2, \dots, N_n) = \prod_{i=1}^n \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \quad (5.6-2)$$

It is now possible to maximize this quantity with respect to the variables N_1, N_2, \dots, N_n , using the method of Lagrangean multipliers, under the restrictions (5.3-22) and (5.3-23). The actual calculations will not be set forth here, but will be left as an exercise for the reader. The result is

$$f(\epsilon_j) = N_j/g_j = \frac{1}{e^{-\alpha} e^{-\beta \epsilon_j} - 1} \quad (5.6-3)$$

This formula is referred to as the Bose-Einstein distribution function. It is again possible to identify β as

$$\beta = -1/kT, \quad (5.6-4)$$

while α may be determined in terms of the number of particles in the system, just as in the Maxwell-Boltzmann and Fermi-Dirac cases. For the case of a continuum of closely spaced levels, $g_j \rightarrow g(\epsilon)d\epsilon$ and $N_j \rightarrow N(\epsilon)d\epsilon$, giving

$$f(\epsilon) = \frac{1}{e^{-\alpha} e^{\epsilon/kT} - 1} \quad (5.6-5)$$

For the independent particle density of states function (5.5-16) for a two-dimensional free particle gas, the parameter α may be explicitly calculated in the same way as ϵ_f for

this system under Fermi-Dirac statistics. It may then be shown that as T becomes large, $\alpha \rightarrow -\infty$, in which case the exponential factor in the denominator of (5.6-5) becomes much larger than unity, and the Bose-Einstein distribution (5.6-5) approaches

$$f(\epsilon) \approx e^{\alpha} e^{-\epsilon/kT}, \quad (5.6-6)$$

which is a distribution function of the Maxwell-Boltzmann type. The same general behavior is obtained for a three-dimensional independent-particle Bose-Einstein gas, although in this case it is not possible to obtain an expression for α in closed form.

In the limit of very high temperatures, the particles of the system will be distributed over a very wide range of energies, and the number of particles in every available energy range will become much smaller than the number of quantum states in that range, whence for all states $g_i \gg N_i$. In this situation, we may write, approximately,

$$\frac{(N_i + g_i - 1)!}{(g_i - 1)!} \approx g_i^{N_i}, \quad (5.6-7)$$

whereby (5.6-2) becomes

$$Q_b(N_1, N_2, \dots, N_n) \approx \prod_{i=1}^n \frac{g_i^{N_i}}{N_i!}. \quad (5.6-8)$$

But this, apart from a constant factor $N!$, is just equal to $Q(N_1, N_2, \dots, N_n)$ as given by (5.3-8) for a Maxwell-Boltzmann system! We should then expect the Bose-Einstein and Maxwell-Boltzmann distributions to coincide in the high-temperature limit on purely physical grounds. The choice of the value given by (5.6-4) for β is thus justified, for this choice, as we have seen above, leads directly to the correspondence between the Bose-Einstein and Maxwell-Boltzmann Statistics shown by (5.6-6).

In the case of the two-dimensional and three-dimensional independent particle Bose-Einstein gases, as the temperature approaches zero, the value of α tends toward zero, the result being that all the particles of the system tend to condense into the lowest energy state of the system at absolute zero. This phenomenon, called the *Bose condensation*, is characteristic of systems obeying Bose-Einstein statistics.

In some applications it is of interest to obtain the Bose-Einstein distribution function without making the restriction that the number of particles in the system be constant. It can be seen from (5.3-15) and (5.3-16) that this result can be obtained from (5.6-5) if α is taken to be identically zero. In this case (5.6-5) reduces to

$$f(\epsilon) = \frac{1}{e^{\epsilon/kT} - 1}. \quad (5.6-9)$$

EXERCISES

1. Show that the wave front associated with the plane wave $\Psi = e^{i(k \cdot r - \omega t)}$ advances along the \mathbf{k} direction.
2. Show for the free particle in three dimensions, whose wave function is given by

(5.2-7) that the expectation value of the vector momentum \mathbf{p} is equal to $\hbar\mathbf{k}$, and that \mathbf{p} (hence \mathbf{k}) is a constant of the motion.

3. Calculate the density of states factor $g(\epsilon)d\epsilon$ for a two-dimensional system of free particles, with instantaneous collision interactions only, contained within a rigid container of area A and dimensions x_0 and y_0 . Start with Schrödinger's equation.

4. Suppose that 4 coins are tossed simultaneously; what are the probabilities associated with the distributions (0 heads, 4 tails), (1 head, 3 tails) ... (4 heads, 0 tails)?

5. Find the dimensions and area of the rectangle of maximum area with sides parallel to the coordinate axes which can be inscribed within an ellipse whose major axis is $2a$ and whose minor axis is $2b$. The axes of the ellipse may be taken to be parallel with the coordinate axes. Use the method of Lagrangean multipliers.

6. Find the root-mean-square speed and the most probable speed of a particle in an ideal Boltzmann gas.

7. Show that the flux of particles in an ideal Boltzmann gas, whose x -components of velocity are positive, per unit area across a plane normal to the x -axis is $\frac{1}{4}N\bar{c}/V$. *Hint:* The flux or current density is defined as the number of particles per unit volume times their velocity component along the normal to the plane across which the flux is observed.

8. Show that the Fermi energy of a two-dimensional Fermi gas of free particles, whose density of states function is given by the result of Exercise 3, is $\epsilon_f(T) = kT \ln(e^{\epsilon_f(0)/kT} - 1)$, where $\epsilon_f(0) = Nh^2/(4\pi mA)$.

9. Calculate the Fermi energy, in electron volts, for the free electrons in copper at absolute zero, assuming one free electron per copper atom. For what temperature would kT be equal to $\epsilon_f(0)$?

10. Show that the internal energy per unit volume of a Fermi gas of free particles at absolute zero is $\frac{3}{5} \frac{N}{V} \epsilon_f(0)$.

11. Show by the method of Lagrangean multipliers that if $Q(N_1, N_2, \dots, N_n)$ is given by Equation (5.6-2), the distribution function corresponding to the most probable values of N_1, N_2, \dots, N_n is given by (5.6-3).

12. Using the density of states function calculated in Exercise 3, show that the parameter α of a two-dimensional Bose-Einstein gas of free particles is given by

$$\alpha = \ln(1 - e^{-h^2 N/(2\pi mA kT)}).$$

Discuss the properties of the resulting distribution function for $T \rightarrow \infty$ and for $T \rightarrow 0$.

GENERAL REFERENCES

- W. Band, *An Introduction to Quantum Statistics*, D. Van Nostrand, Princeton, N.J. (1955).
- R. W. Gurney, *Introduction to Statistical Mechanics*, McGraw-Hill Book Co., Inc., New York (1949).
- D. ter Haar, *Elements of Statistical Mechanics*, Holt, Rinehart and Winston, Inc., New York (1954).
- R. B. Lindsay, *Introduction to Physical Statistics*, John Wiley and Sons, New York (1941).
- J. E. Mayer and Maria Göppert-Mayer, *Statistical Mechanics*, John Wiley and Sons, New York (1940).
- R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938).